The Measurement of Osmotic Pressure and its Application to a Study of Aqueous Phenol Solutions

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

ARTHUR GROLLMAN

BALTIMORE

June, 1923

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TABLE OF CONTENTS

Acknowledgment 4

I. Improvements in the Mode of Measurement of Osmotic Pressure:

Introduction 5

The Cells and Membrane:

Preparation of the Cells 6
Relation of Cell and Membrane 6
Cell Filling 7
Membrane Deposition 8
Discussion of the Cells 8

A New Interferometer Cell for Use as a Pressure Gage:

The Measurement of Pressure 9
Description of the Instrument 9
Cross Section of Pressure Tube—Plate 1 7
The Accuracy of the Instrument 10

Conclusion 10

Summary 11

II. The Osmotic Pressures of Aqueous Phenol Solutions at 30° C.:

Introduction 11

Experimental Results:

Method Employed 12
Results, Table I 12

Discussion of Results:

Comparison with Theoretical, Table II 13
The Degree of Association of Phenol 15

Effect of Temperature on the Association of Phenol 15

Summary 16

Biography 17

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I.

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE

Introduction

Of the various experimental physicochemical methods, none is of greater importance than the measurement of osmotic pressure. The thermodynamic considerations of solutions are based on the concept of an osmotic pressure and all other properties of solutions are derivable from osmotic-pressure data. Of paramount importance is the fact that osmotic-pressure measurements are capable of the greatest refinement, being measurable with an extreme accuracy. Though we possess other accurate means of measurement such as of the freezing point and the vapor pressure, these are very limited, the former being confined to one temperature, the latter applicable over only a limited range of temperature. Osmotic-pressure measurements, on the other hand, can be carried out with equal precision over the range of temperature in which the solvent in question exists in the liquid form and throughout all possible concentration limits.

Despite these desirable conditions and advantages, measurements of osmotic pressures have been limited to a few substances, such as sugar and glucose. Substances of lower atomic weight, and especially electrolytes, have defied measurement and it has usually been assumed in the case of electrolytes that measurement is impossible because of the destructive effect on the semipermeable membrane and the permeability of the latter to such substances. The object of this investigation was so

to modify the present mode of measurement as to make it more widely applicable and, if possible, to apply it to the measurement of electrolytes.

The Cells and Membranes

Of primary importance in the experimental determination of osmotic pressure is the character of the clay cell used as the support of the semipermeable membrane. Indeed, the lack of cells of proper texture was the cause of failure by early investigators. The cells used by Morse and Frazer in their work were made with every precaution to obtain a final product having a uniform porosity, a fine structure, and lacking, above all, any "air blisters." Such cells were obtained in the laboratory by carefully elutriating and washing the clays, pressing the obtained mixture, and finally turning to the required form on the lathe, after which the cell was baked and its collar glazed. The microscopic structure of such a cell (Type A) showed that it had a fine and uniform texture.

Since the function of the cell in measurements of osmotic pressure is to secure a support for the membrane to be used, it is perfectly obvious that the fineness of texture of the latter will depend entirely on the size of the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely, and the exertion of any pressure at this point would easily disrupt it.

The failure of early attempts to measure the osmotic pressure of solutions of electrolytes was usually attributed to the destructive effect of the electrolytes on the colloidal nature of the copper ferrocyanide membrane. To be sure, this is an important factor in such determinations, but it appeared likely that the failure of early attempts was due also, in a large measure, to the character of the cell itself. The fact that only substances of high molecular weight could be studied while other materials of molecular weights of a lower magnitude including electrolytes, passed through the semipermeable membrane suggested that cells of a finer structure might support membranes of a finer structure which, though incapable of prolonged existence in the presence of disrupting agencies would, nevertheless, prevent leakage of the solute and thus serve as true semipermeable materials for the period of time required to make a measurement.

To obtain cells with a texture finer than the one described above by the same method is scarcely possible. This cell was subjected during preparation to a pressure of about 3000 kg. per sq. cm. of surface of clay for 15 hours. Moreover, as shown later, cells of any appreciable thickness of finer texture than shown by Type A, although capable of supporting a membrane impervious to the solute would, nevertheless, fail to give accurate osmotic-pressure measurements. It was decided, there-

fore, to produce in the cells heretofore used some insoluble material which would give a support for the membrane. Microphotographs of cross sections of cells so prepared (Types B, C, D and E) showed darker areas representing the areas where the interior of the cell had been modified by the introduction of these fillings, whose extremely fine structure was indicated by the opacity to light which these sections showed under the microscope.

The Type B cell was filled with magnesium silicate by electrical diffusion. The cell to be treated was placed in an apparatus similar to that used in depositing the membrane, and a current (taken directly from the lighting circuit) passed between a roll of platinum foil placed within the cell, which served as the anode, and a foil (2 cm. wide) which surrounds the cell, dilute solutions of magnesium nitrate and sodium silicate serving as anolyte and catholyte, respectively. In this manner the required filling can be obtained in any thickness required, depending on the period of deposition. The

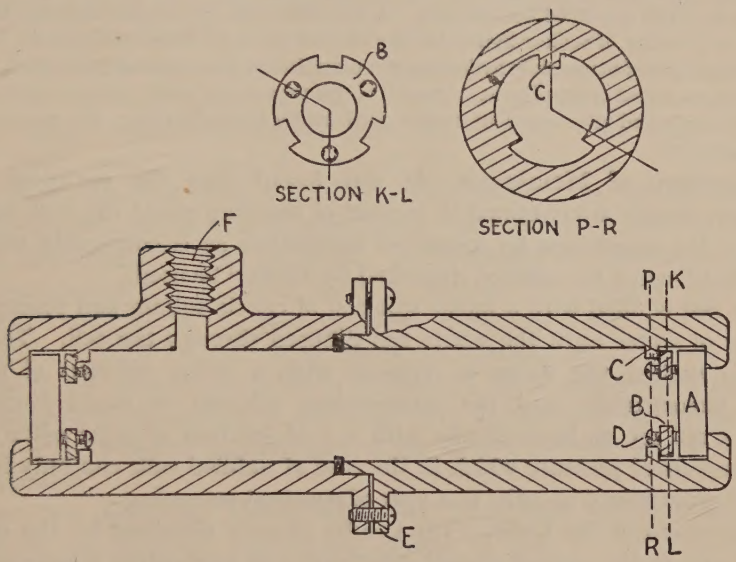

Fig. 1

optimum results are obtained with an electrolysis of about 10 hours. The initial amperage, which varies with the porosity of the cell in question, ranged from 0.5 to 1 ampere under the above conditions and drops in 10 hours to 0.02–0.2 amperes. It was found that cells filled in this manner scarcely cracked on baking and gave most efficient results. After all treatments, the cells are baked in a pottery kiln for several days at 1000–1450° and then, after thorough electrolysis with a 0.05% lithium sulfate solution to remove all air from the cell by endosmosis, the cell is electrolyzed with pure water until all electrolytes have been removed. It is then ready for the deposition of the membrane.

Type C cell was filled in a similar manner, except that sodium hydroxide was used instead of the silicate and the magnesium hydroxide thus formed was burned in the kiln. The filling was rather narrow and not at the very surface of the cell, but toward the interior.

Type D was filled exactly as was Type E cell but was not baked after filling. This was made evident in the photographs by the greater porosity of the baked cell due to the

contracting effect of heat on the filling. The baked cells invariably gave better results, which may be explained by the fact that too dense or too thick a filling does not allow free and easy diffusion of solvent through the cell which, in turn, results in a slow and incomplete attainment of equilibrium, despite the fact that with such cells no leakage or a negligible amount occurs.

Type E cell contained a filling of magnesium silicate produced as follows. The cell was placed in a solution of concentrated magnesium chloride which diffused and thoroughly filled the pores of the cell. After the outer surface had been washed, the cell was transferred to a solution of sodium hydroxide which on diffusion precipitated magnesium hydroxide in the cell. In order to produce a more insoluble filling, this was converted to the silicate by boiling in a 10% solution of sodium silicate. The above process was repeated several times until no more "filling" could be inserted. The "filling" was precipitated at the outer surface of the cell where it was desired, since it is here that the membrane is deposited. The main objection to this method of cell treatment is the fact that the majority of cells so treated crack on drying.

Type F cell was filled by diffusion. A cell filled with magnesium chloride and inserted in a beaker of sodium hydroxide was allowed to stand for several weeks. In this way a fine layer of magnesium hydroxide was precipitated where the solutions met, which was then converted to the silicate. One cell of this type was actually used in quantitative measurements and gave excellent results until finally it cracked from the pressure developed in use.

Deposition of Membrane.—It was found that the optimum and quickest results are obtained if, instead of bringing about the first deposition of the membrane by means of electrolysis as is commonly done, a modified form of the method described by Pfeffer[1] be used.

The cell is filled with a molar solution of cupric sulfate and placed in a beaker of water until the solute has diffused through the cell. The cell is then washed, the water is replaced with a molar solution of potassium ferrocyanide, and the arrangement allowed to stand overnight. Such a cell set up immediately with a 2 *M* solution of sugar often gives the theoretical pressure which in the case of unfilled cells can only be obtained after from 6 months to a year of constant seasoning.

Discussion of the Cells.—The results already obtained by the use of filled cells in the case of phenol solutions[2] and qualitative measurements made, show that the above method of cell treatment accomplishes its purpose. Regardless of the magnitude of the molecular species under consideration, the leakage in any case is but minimal. However, it cannot be too strongly emphasized that non-leakage is not to be taken as a criterion of a successful measurement, as has been done by some investigators. The only criteria for a good measurement are the attainment of a pressure which remains constant for some time, non-leakage of solute and, above all, the ability to duplicate all results with other cells and measuring apparatus, in so far as the limit of accuracy of the method permits. Data based on measurements not fulfilling these requirements are to be considered worthless.

[1] Pfeffer, "Osmotische Untersuchungen," **1877.**

[2] Grollman and Frazer, *J. Am. Chem. Soc.*, **45**, 1705 (1923).

Another point of superiority of the filled cells is the speed with which they attain equilibrium, which far exceeds the time required with unfilled cells. Indeed, measurements of 50 atmospheres' pressure have been attained with sugar solutions, using air manometers, within 20 minutes after setting up, and the fact that in such measurements a considerable diffusion of solvent must take place to produce the pressure, shows the potency of the force with which we are dealing.

A New Interferometer Cell for Use as a Pressure Gage

Besides the question of cells, whose improvement has been discussed above, the mode of measuring the pressure exerted is of fundamental importance. Nitrogen-filled manometers which have been used in the past have the great disadvantage that the time for equilibrium is rather long, since for its attainment, considerable solvent must pass through the cell. With electrolytes it is essential to make rapid determinations, since long contact with the solutions has a detrimental effect on the membranes. Hence, a more rapidly registering pressure gage was desired. Van Doren, Parker and Lotz[3] have devised a method of measurement in which the change of refractive index with pressure as measured by the Zeiss water-interferometer serves as a pressure gage. By the use of this instrument rapid determinations can be made. As developed by these investigators the instrument has, however, several defects. It is rather difficult to assemble, leakage at the glass windows being especially hard to avoid. Moreover, due to the manner in which the windows are held in place, the length of the pressure chamber is necessarily made small, which means a corresponding diminution in the sensitivity of the instrument, the sensitivity being directly proportional to the length of the column of liquid compressed.

The two objections mentioned above have been satisfactorily overcome by the modified instrument shown in Fig 1. This new form combines ease of assemblage and high sensitivity, the latter being twice that of the original instrument. As it is generally applicable wherever pressure measurements are to be quickly and accurately made, it will be briefly described.

It consists essentially of a brass tube, with optical glass windows inserted at its ends, which is held in place by means of a square block of brass through which are drilled 2 holes. One of these serves to hold the pressure chamber in place, while the other, which is contiguous to the first, holds the other window which, dipping into the water-bath of the interferometer, serves as the non-pressure or comparison chamber. By this arrangement only the pressure tube requires especial care in construction to avoid leakage, and it is this simplification which gives the instrument both ease in assemblage and greater accuracy. A plate screwed on the end blocks serves as a support of the chambers in the bath. Since the parts on being assembled assume the same relative position, no diffi-

[3] Van Doren, Parker and Lotz, *J. Am. Chem. Soc.*, **43**, 2497 (1921).

culty is experienced by a change in the zero reading of the instrument such as would occur were the arrangement not exactly reproducible.

In order to introduce the glass windows into the ends of the pressure chambers from the inside, thus giving a tighter joint between glass and metal with increasing pressure, the pressure tube must be made in two parts. These are joined by the flange arrangement E, leakage being prevented by insertion of a washer made of steam packing where the two ends meet within the tube. Such washers do not flow under pressure as ordinary rubber does. The tube, which is otherwise of uniform bore throughout its length, has 3 points of projection, C, which serve to support the washer B. The glass windows, A, are circular, but have 3 notches corresponding to the 3 projections from the tube, in order that the windows may be slipped past these projections. After the windows are introduced as shown in the figure, a circular brass washer, B, having notches similar to those of the glass plate, is slipped beyond the projections, turned so that it is now supported by the projections, C, and the glass windows are held tightly against their supports by means of the screws, D. The windows are made air-tight by the use of a rubber solution which, after assemblage, is vulcanized by slow heating. The tube is joined by F to a mercury trap which in turn is connected to the pressure cell or to the source of the pressure to be measured.

The instrument as described above has a range of 30 atmospheres. This can be increased as described by Van Doren, Parker and Lotz[3] by the use of thin glass plates inserted in the path of the beam passing through the non-pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions, the pressure readings are accurate to 0.1 of an atmosphere. The accuracy can be further increased by using a more compressible liquid than water in the instrument and interferometer bath and by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument as described above was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage, which insures more accurate readings.

For a complete description of the use of the interferometer, the reader is referred to the papers[4] by Adams, Cohen and Bruins, Löwe, and Haber and Löwe.

Owing to the difficulties inherent in most methods of pressure measurements, their limited applicability and accuracy, the use of the water interferometer should prove itself a most desirable substitute for certain methods heretofore employed.

Conclusion

It is hoped that with the modifications above described, the road is paved for the measurement of the osmotic pressure of electrolytes and other substances whose behavior in solution, as shown by the osmotic pressures

[4] Adams, *J. Am. Chem. Soc.*, **37,** 1181 (1915). Cohen and Bruins, *Z. physik. Chem.*, **103,** 337 (1923). Löwe, *Chem.-Ztg.*, **51,** 405 (1921). Haber and Löwe, *Z. angew. Chem.*, **23,** 1393 (1910).

which they exert, may throw light on the important questions of solutions. Qualitative results obtained with lithium chloride, sodium nitrate, sodium acetate, cupric chloride, sodium chloride, ethyl alcohol and acetic acid are promising and though no successful quantitative results with concentrated solutions have as yet been obtained, experiments on the more dilute solutions are now in progress, the results with phenol having already been published.

Summary

1. The method of experimentally determining osmotic pressures has been improved by filling with various silicates the cells on which the membrane is precipitated.

2. Such cells are efficient supporters of the membrane, allow but a minimal leakage, a rapid attainment of equilibrium, and do not require long seasoning.

3. An interferometer cell has been devised which is capable of acting as an accurate and rapid pressure gage.

II.

THE OSMOTIC PRESSURES OF AQUEOUS SOLUTIONS OF PHENOL AT 30°

Introductory

The only reference to be found in the literature of an attempt to determine experimentally the osmotic pressure of phenol solutions is that of Naccari,[5] whose results, being much lower than those theoretically expected and incapable of either duplication or accurate determination, were rejected by Naccari as unsatisfactory. Owing to the crudity of the method employed, which at its best could give but qualitative results, his data are of interest only from an historical standpoint.

[5] Naccari, *Atti. accad. Lincei*, **6**, 32 (1897).

Indeed, even with the experimental refinements of the later methods as developed by Morse and Frazer, and their co-workers, only such compounds as the sugars were capable of accurate measurement. Failure to obtain results with substances of a low molecular weight were attributed to permeability of the cupric ferrocyanide membrane, or to the disintegration of the latter in the presence of such substances. Recent improvements in cell structure, which have been made in this Laboratory, have enabled the methods of direct osmotic-pressure measurements to be applied to a variety of substances hitherto considered beyond experimental determination, with an accuracy comparable to that of the best results obtained with cane sugar.

Phenol, presenting as it does rather anomalous behaviors in aqueous solution, was chosen for measurement, to determine whether the results so obtained could be correlated with its other properties. The great uncertainty existing regarding certain of its actions, such as cryoscopic behavior, hydration, etc., demanded an attack from another point of view in order to throw light on these subjects. The fact that it forms solutions with two coexisting phases was also suggestive. Moreover, all substances hitherto measured have approximated ideal solutions and obey the van't Hoff osmotic-pressure formula more or less closely. Phenol was, therefore, chosen, as it diverges widely from such behavior.

Experimental Part

The measurements were carried out throughout the solubility range at 30°, with nitrogen-filled manometers in a bath constant to 0.05°. The method was essentially that described and used by Frazer and Myrick[6] for sugar solutions, manometers being used, however, instead of the resistance gage there described. For low pressures, the manometric method is the most accurate though not the most convenient mode of measurement.

The solutions were analyzed with a Zeiss water-interferometer which permitted an accuracy exceeding that required by the manometric readings with a cathetometer.

The cells were perfected in a manner to be described in a later article;

TABLE I

RESULTS

Concn. of phenol per 1000 g. of H_2O Moles	O. p. obs. Atm.	Ratio: o. p. to concn.	Concn. of phenol per 1000 g. of H_2O Moles	O. p. obs. Atm.	Ratio: o. p. to concn.
0.0986	1.42	1.45	0.2965	3.89	1.31
.1006	1.47	1.46	.3831	4.90	1.28
.1992	2.73	1.42	.5214	6.67	1.28
.1999	2.83	1.42	.6672	8.42	1.26
.2716	3.73	1.37	.8936	11.20	1.25

[6] Frazer and Myrick, *J. Am. Chem. Soc.*, **38**, 1907 (1916).

upon them were deposited the usual membrane of cupric ferrocyanide. These allowed but a slight permeability of the phenol, which was finally corrected for by analysis of the solutions. Equilibrium was obtained in less than 6 hours, even with the most concentrated solutions.

Table I and Fig. 2 give the results obtained. The curve is practically linear, tending to slope slightly towards the X axis with increasing concentration. The third and sixth columns show this tendency.

From the equation for ideal solutions,

$$P = \frac{RT}{V_0}\left(x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \ldots\ldots\right) \qquad (1)$$

where P is the osmotic pressure, V_0, the molecular volume of solvent and x, the molar fraction of solute, we can, neglecting the association of water,[7]

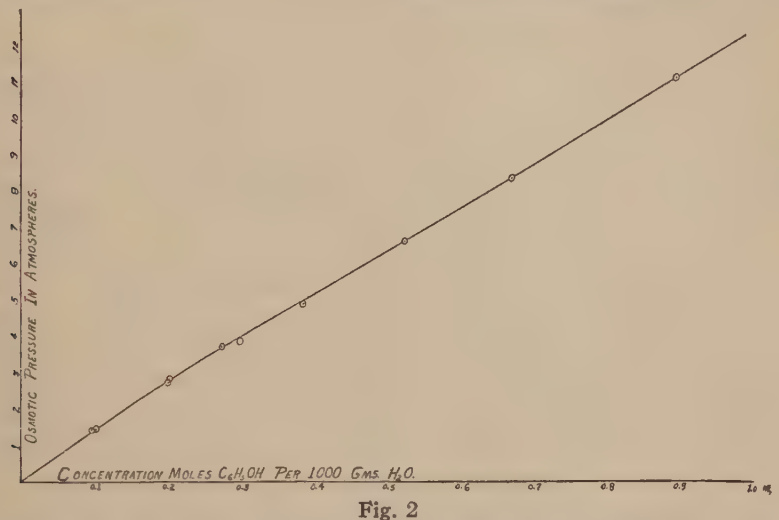

Fig. 2

calculate the theoretical osmotic pressures of phenol solutions. This has been done in Cols. 2 and 6 of Table II. By interpolation of the observed values in Table I, the values for exact concentrations are obtained in Cols. 3 and 7.

TABLE II

COMPARISON OF THEORETICAL WITH EXPERIMENTAL RESULTS

Concn.	O. p. calc. from Formula I	O. p. obs.	Calc. o. p. / Obs. o. p. degree of assoc.	Concn.	O. p. calc. from Formula I	O. p. obs.	Calc. o. p. / Obs. o. p. degree of assoc.
0.1	2.46	1.46	1.68	0.6	14.73	7.62	1.93
.2	4.92	2.84	1.73	.7	17.16	8.82	1.95
.3	7.38	3.93	1.88	.8	19.59	10.05	1.95
.4	9.83	5.12	1.92	.9	22.02	11.28	1.95
.5	12.28	6.40	1.92	...	..	...	..

[7] Kendall, *J. Am. Chem. Soc.*, **36**, 1222, 1722 (1914); **37**, 149 (1915); **38**, 1309, 1712 (1916); **42**, 2131 (1920).

A comparison of the observed values in Cols. 3 and 7 and the theoretical values calculated in Cols. 2 and 6 shows, as Cols. 4 and 8 indicate, that the former are approximately $^1/_2$ the latter, thus showing the probability of association of 2 molecules of phenol in aqueous solution to form a diphenolic complex.

If α is the degree of association of phenol, we must introduce this factor in Equation 1. Assuming the association to take place exclusively according to the equation, $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$, instead of C, the molar concentration, we must use $\frac{\alpha c}{2} + (1-\alpha)c$ or $c\left(1-\frac{\alpha}{2}\right)$ and x, the molar fraction, becomes $\frac{c\left(1-\frac{\alpha}{2}\right)}{55.5 + c\left(1-\frac{\alpha}{2}\right)}$

Making these substitutions in Equation 1 and substituting for the osmotic pressure, P, the observed values, we are able to calculate, α, the degree of association at the various concentrations. The decrease in the relative osmotic pressures with increasing concentrations is due to an increase in the degree of association of phenol with higher concentrations. The value of α increases from 86% for 0.1 M to 99% for 0.9 M solutions.

Beckmann and Maxim[8] have derived values for the association of phenol in carbon tetrachloride and bromoform in various concentrations and at temperatures varying from the freezing points of the above-mentioned solvents to their boiling points under normal pressure. The degree of association is found to be most sensitive to dilution, rising for example from the value 1.21 for a solution of 0.599 g. of phenol in 100 g. of carbon tetrachloride at 54.1° to the value 1.58 when the same amount of solvent contains 2.738 g. The results in Table II, Cols. 4 and 8, derived from the osmotic pressure studies, lead us to the same conclusion, namely, that dilution is a potent factor in decreasing the association of phenol. This decrease of association with dilution may explain the great variance in the behavior of phenol in aqueous solutions on bromination. The formation of tribromophenol and tribromophenol bromide (tetrabromocyclohexadienone) may be due to the presence of both the simple molecule and the associated form in solution. Attention may be called to alternative explanations of the above phenomena, as due to the presence of a quinoid form,[9] or as due to the presence of hydrobromic acid.[10]

The Association of Phenol

The above conclusion that phenol exists in solution in an associated form is supported by its behavior in other respects, both physical and

[8] Beckmann and Maxim, *Z. physik. Chem.*, **89**, 411 (1915).

[9] Dinwiddie and Kastle, *Am. Chem. J.*, **46**, 502 (1911).

[10] *J. Chem. Soc.*, **121**, 2810 (1922).

chemical. Essex,[11] from a study of the compressibility of phenol, applied the principle of Tammann[12] whereby molecular magnitudes of anisotropic phases are determined, and finds that phenol exists as two forms of $(C_6H_5OH)_2$, a third species —C_6H_5OH— being enriched at higher temperatures. Turner and English[13] found, by a study of the freezing points in benzene, that the molecular weight of phenol varies from 149.6 to 194.5; these results are in the same order of magnitude as those derived from the osmotic-pressure measurements. Walden,[14] by a study of the specific cohesion, reaches the same conclusion. The surface-tension measurements of phenol solutions,[15] cryoscopic measurements, etc., all point to association of phenol.

In its chemical reactions, also, phenol shows a tendency towards reacting not as a simple molecule but rather in an associated form. Thus the following compounds have been isolated: $2C_6H_5OH.H_2O$;[16] $2C_6H_5OH.TeCl_4$;[17] a series of compounds having the structure $2C_6H_5OH.Ca(OH)_2 \; x \; H_2O$;[18] $(C_6H_5OH)_2H_2SO_4$;[19] as well as numerous other addition products. In all of these compounds 2 molecules of phenol react, which points to the probability that phenol reacts as the dimolecular compound —$(C_6H_5OH)_2$, as indicated by the values of the osmotic pressures.

Effect of Temperature on the Degree of Association

Solution of phenol is accompanied by a large absorption of heat. The measurements of various properties, such as ebullioscopic, etc., all give results indicating a decrease in the degree of association with increasing temperature. Applying the Le Chatelier principle, it is obvious that the compound formation must be exothermic and, *vice versa*, the dissociation of the double molecule takes place with an absorption of heat. We must, therefore, attribute the negative heat effect resulting on dissolving phenol as due to the breaking down of the more complicated structure with the formation of a certain percentage of simple molecules. The pure substance, therefore, exists practically entirely in an associated form; experimental studies of the molten material corroborate this (as, for example, Essex's work quoted above).

[11] Essex, *Z. anorg. Chem.*, **88**, 189 (1914).

[12] Tammann, *Z. physik. Chem.*, **84**, 293 (1913).

[13] Turner and English, *Proc. Roy. Soc.*, **105**, 1786 (1914).

[14] Walden, *Z. physik. Chem.*, **65**, 189, 266 (1908).

[15] Morgan and Egloff, *J. Am. Chem. Soc.*, **38**, 844 (1916). Feustel, *Ann. Physik*, [4] **16**, 61 (1905).

[16] Smits and Maarse, *Proc. acad. Sci. Amsterdam*, **14**, 192 (1911). Rhodes and Markley, *J. Phys. Chem.*, **25**, 527 (1921).

[17] *Ber.*, **30**, 2832 (1898).

[18] *J. Russ. Phys. Chem. Soc.*, **45**, 1535 (1914); *Chem. Centr.*, **1914**, I, 110.

[19] *J. Am. Chem. Soc.*, **36**, 2507; *ibid.*, 1222 (1914).

Summary

1. The osmotic pressures of phenol solutions have been determined throughout the solubility range at 30.0°.

2. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the dimolecular form varies from 86% for 0.1 *M* solution to 99% for 0.9 *M* solution. The pure material is entirely associated.

3. It is suggested that the variance in the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is attributable to the different molecular combinations present.

4. The great absorption of heat attending the solution of phenol is due to the partial decomposition of higher molecular forms, the reaction $(C_6H_5OH)_2 \longrightarrow 2C_6H_5OH$, being endothermic.

BIOGRAPHY

Arthur Grollman, the author of this dissertation, was born at Baltimore, Md., on October 21, 1901. After graduation from the Baltimore City College, he entered the Johns Hopkins University in the fall of 1918, receiving the degree of B.A. in 1920. He entered the Graduate Department of Chemistry in the fall of the same year, taking Physical Chemistry and Mineralogy as subordinate subjects. He was a recipient of Hopkins Scholarships for the years 1918–1923 and was assistant in the physical chemistry laboratory during the spring of 1923.